THE EFFECT OF CHEMICALLY MODIFIED LIGNIN AS A FILLER IN ULTRAVIOLET CURABLE RESIN SYSTEM

by

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Thesis submitted in fulfillment of the
requirements for the Degree of
Master of Science

June 2011

ACKNOWLEDGMENT

Firstly, I would like to express my utmost appreciation to my main supervisor Professor Rozman Hj Din and my co-supervisor Dr Tay Guan Seng for all their advice and guidance throughout the course of this project. A lot of insights and tutelage had been generously given by them. Without their encouragement and assistance, this research would not have been completed in timely manner.

I would also like to extend my appreciation to my research friends for encouragements to complete this challenging research. I am indebted to their suggestions and support along this research. Once again I would like to thank all my friends who have helped me directly or in directly and my apologies goes to those whose name not mentioned here.

Besides, I would also like to convey special thanks to the coatings Laboratory Assistants, Encik Ahmad Yahya, Puan Noraida BuKhari and Encik Shamsol Zoolkifli, for their cooperation and help during my research. Without their help, I would not able to complete my research.

Finally, at my personal level, I am grateful to my family members and my friend for their unstinting support.

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LIST OF ABBREVIATIONS

%	Percentage
ADPPH	Absorbance of the DPPH solution
AGE	Allyl glycidyl ether
ANOVA	Analysis of variance
AS	Absorbance of the solution
ASTM	American society for testing material
C = C	Unsaturated group
DPPH	2, 2-diphenyl-1-picrylhydrazyl
EFB	Empty fruit branches
FTIR	Fourier transform infrared spectroscopy
GMA	Glycidyl methacrylate
M	Monomer
PI	Photoinitiator
$R_1^{\bullet}$, $R_2^{\bullet}$	Radical fragments of the photoinitiator
$R_3 - H$	hydrogen donor
RSA	Percentage of DPPH discoloration
UV	Ultraviolet
VOC	Volatile organic compound
WPG	Weight percentage gain

KESAN LIGNIN TERAWAT SEBAGAI PENGISI DALAM SISTEM TERMATANG SINARAN ULTRAUNGU

ABSTRAK

Alcell lignin telah digunakan sebagai pengisi dan komponen reaktif dalam sistem pempolimeran sinaran ultraungu (UV). Dalam kajian awal, parameter-parameter seperti jenis fotopemula dan peratusan fotopemula yang diperlukan telah dikaji. Daripada keputusan, didapati fotopemula radikal bebas adalah lebih berkesan daripada fotopemula kationik dalam pematangan resin yang terisi lignin Alcell. Seterusnya, kesan peratusan Alcell lignin yang berbeza dalam resin terhadap sifat filem yang terhasil telah dikaji. Daripada keputusan, didapati kehadiran lignin telah meningkatkan kekerasan filem sehingga mencapai ke titik ambang (10%), sebelum menurun. Fenomena ini disebabkan oleh jumlah resin yang bertindak sebagai matriks tidak mencukupi untuk memegang lignin sebagai pengisi dalam sistem. Bagi memperbaik keserasian lignin dengan matrik, perawatan lignin telah dijalankan dengan menggunakan glisidil metakrilat (GMA) dan allil glisidil eter (AGE). Keputusan perawatan lignin menunjukkan peningkatan nisbah reaktan kepada lignin akan meningkatkan penambahan peratusan berat (WPG). Maka, pemerhatian ini dapat dikatakan bahawa interaksi antara lignin dan reaktan telah berlaku. Penentuan nombor iodin lignin juga dijalankan dan menunjukkan corak keputusan keputusan yang sama dengan WPG. Hal ini menunjukkan kumpulan ikatan C=C telah bertambah dengan peningkatan WPG. Keberkesanan lignin sebagai pengisi dalam sistem termatang UV telah dikaji melalui kekuatan tensil, modulus tensil, perpanjangan pada takat putus, kandungan gel, kekerasan pendulum, perekat menetas lintas, ketahanan lelasan. Keputusan menunjukkan bahawa pencampuran lignin (terawat atau tidak terawat) dalam sistem termatang UV mempengaruhi sifat filem penglitup.

THE EFFECT OF CHEMICALLY MODIFIED LIGNIN AS A FILLER IN ULTRAVIOLET CURABLE RESIN SYSTEM

ABSTRACT

Alcell lignin was used as filler and reactive component in a ultraviolet (UV) curable system. In the preliminary study, different parameters have been used such as type of photoinitiator, percentage of photoinitiators and to determine suitable photoinitiator in the presence of lignin. The results showed gel content of the film of free radical photoinitiator has higher efficiency than cationic photoinitiator. Subsequently, the effect of lignin content in UV curable system was studied. The results indicated that the hardness of film increase as the lignin content was increased to the optimum point (10%), after which it decreased. This phenomenon may due to the insufficient resin or oligomer to act as matrix to hold the lignin as filler in the system. In order to enhance the interfacial of lignin and matrix of resin, chemical modification of lignin has been carried out with glycidyl methacrylate (GMA) and ally glycidyl ether (AGE). The result indicated that the increase the ratio of the reactant to lignin could increased WPG. It can be said that interaction between lignin and reactant has occurred and more unsaturated groups have been added in lignin molecule. Iodine number determination of modified lignin was carried out the similar trends observed with WPG result. The effect of lignin as filler and reactive component in ultraviolet curable resin systems were investigated by tensile strength, tensile modulus, elongation at break, gel content, pendulum hardness, cross hatch adhesion, abrasion resistance and Fourier transform infrared spectroscopy (FTIR). In addition to that, weight percentage gain (WPG) and iodine number was used to study the modification effect of lignin.

CHAPTER 1 INTRODUCTION

1.1 Introduction

According to Dufour et al. (1991), in 1971 ultraviolet (UV) curing was commercially used in Japan printing industry. The initial use of this curing technique was mainly from entrepreneurial printers. Shortly this technology became the public knowledge and started to expand rapidly in the mid 80' as the quantity of people and companies involved in UV curing increased.

In 21st century, environmental economy and energy usage have received a lot of attention. According to Burak (1997), government around the world are passing legislation mandating tougher controls on volatile organic compound (VOC) emissions. UV curing fulfils with all of these environmental regulations due to its solvent-free and usually VOC-free, depending on the volatility of the monomers used and low energy consumption (Dufour et al., 1991). As a result, radiation curing technology is very attractive to manufacturers of all kinds of products and low energy consumption.

Throughout 25 years, radiation curing and technology have gone from a subject of exclusive research specialities into a major industrial development and is now a field of central importance in polymer science and technology (Allen, 1996). UV applications include resists, barrier coatings, paper, board and metal coatings, dentistry, imaging science and printing. Inherent of these technologies is the use of photoactivator systems (which is named as photoinitiator) and it capable of absorbing UV radiation wavelength.

Biomass is defined as wastes from plant and animal which is the organic matter on earth and in the ocean. According to Hall (1981), biomass is made up of products, co-products, refuse and wastes of plants, animals and people. Basically biomass can be found in agriculture, silviculture and aquaculture and usable for several applications such as food, feed, fiber, feedstock, fertilizer and fuel. Therefore, biomass must be harvested or collected, assembled, often compressed, transported and stored for use (Hall, 1981). According to Demirbas (2005), the components of biomass include cellulose, hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, starches, water, ash and other compounds. Biomass energy is defined as the solar energy, which is stored in plants and animals or in the wastes and this energy can be recovered by burning of biomass as fuel. Biomass can be used directly in energy application through burning without chemical processing.

Filler are solid substances that can be added in high percentage to plastic, paints and paper that could adjust volume, weight costs or technical performance. According to Zweifel et al (2009), filler is defied as solid materials that able to significantly affect certain properties of a base material because of their physicochemical constitution. Generally, filler can interact with the base material, where by, the filler surface has to be more in contact with the matrix (Zweifel et al., 2009).

In Malaysia, the rapid expansion of oil palm plantation in our country has generated enormous amounts of bio-waste. This creates problem in replanting operations and raises tremendous environmental concerns. For the past few years, it was reported that Malaysia has produced about 70 million tonnes of oil palm

biomass, including trunks, fronds and empty fruit branches (EFB) (Joshua Foong, 2011). According to Nerenberg (2011), there were 20.0 million tonnes of EFB was produced in 2011. EFB has traditionally been incinerated and their ash recycled back to the plantation as fertiliser. However, owing to the pollution problem, incineration of EFB has been discouraged. Thus, many attempts have been carried out to convert this by-product into value added materials.

Pulping is the process of converting wood or lignocellulosic material into pulp for papermaking. During this process, fibres are separated by dissolving lignin that serves as a natural adhesive in fibre bundles. The used liquor consists of lignin that can be extracted and used as raw material for value-added product preparation. Lignin is the most abundant organic polymer on earth after cellulose (Dao, 1987; Filley et al., 2002). The lignin molecule consists of various types of substructures that appear to repeat in a haphazard manner.

Lignin has been commonly used in the study of polymer preparation such as polyurethane and polyester preparations. Sun et al. (2007) prepared epoxy resin from lignin and Bonini et al. (2005) reported that lignin from straw could be used as a raw material for polyurethanes preparation which was suitable for wood adhesive formulation. In addition, they also utilized lignin in polyester synthesis for polyurethane coatings formulation. Thielemans and Wool, (2005) used kraft lignin to treat flax fibre for composite preparation. The results showed that the fibre wettability was improved and the mechanical properties of the composite prepared were enhanced. Many efforts also have been made to understand the relationship between structure and properties of these lignin macromolecules in order to find out

more noble applications. For instance, it is commonly used as a raw material in making coatings due to their small particle size, hydrophobic behaviour and the ability to form a stable mixture with other components (Park et al., 2007).

Recently, antioxidant properties of lignin are one of the focuses in the area of lignin utilization research. The scavenging action of lignin phenolic structure on oxygen containing reactive free radicals is considered (Dizhbite et al., 2004). In ultra-violet (UV) curing system quenching phenomenon is one of the undesired reactions where the free radicals generated by photoinitiator are terminated by oxygen. Commonly, this phenomenon can be prevented using several solutions, such as nitrogen blanketing or increase the percentage of photoinitiator. It was previously know that with the antioxidant properties of lignin, lignin may not be cure in UV curing system. However, the quenching phenomenon only affect to the oxygen induce free radical photoinitiator. Hence, it is believed that free radical that generate by alpha hydroxyketone is not be affected by the quenching effect.

This research study was separated into two phases which phase I was preliminary studies on the effect of lignin incorporation into UV curable system on various aspects. By incorporating lignin in the UV-curable resin, interaction between lignin and acrylic oligomer could be triggered. This may increase the hardness of the coatings, which can be reflected in the physical and mechanical properties of the produced coatings. In addition, it is also believed that with antioxidant properties of lignin, the quenching phenomenon can be avoided.

Subsequently, in phase II, chemical modification of lignin with Glycidyl Methacrylate (GMA) and Ally Glycidyl Ether (AGE) would be carried out. The main objective of this chemical modification was to enhance the interaction between lignin and oligomer.

1.2 Objective

- To use lignin as a filler in UV curable system.
- To investigate the effect of the lignin content on UV curable system.
- To study the effect of chemical modification of lignin on the film properties produced by UV radiation.

CHAPTER 2 LITERATURE REVIEW

2.1 UV curable systems

An ultraviolet (UV) and electron beam (EB) curing technology was commercially introduced in 1960s (Mauguière-Guyonnet et al., 2006). UV radiation is used to induce photochemical polymerization or cross linking of monomer, oligomer or prepolymers, which commonly consist of unsaturated groups such as acrylic groups with the containing of an appropriate initiator. UV curing system is defined as the fast transformation of 100% reactive, specially formulated liquids into solids by UV photons or electron. This definition is referred to the well-known fact that organic molecules become electronically excited or ionised after energy absorption (Mehnert et al., 1998).

According to Allen (1996), certain types of UV light-curable monomers and prepolymers have been developed to produce molecules that contain unsaturation and are capable to react with other unsaturated molecules to produce a solid coherent film when subjected to UV light energy. In the industry, diluents monomers have been used and are divided into first generation and second generation types (Allen, 1996). The first generation type is typical mono- and difunctional structures, such as methyl methacrylate and styrene. Whereas, second generation type is usually di- and multifunctional acrylate such as glycerol propoxylate triacrylate. The former type is now infrequently used due to their strong odour, toxicity and slow speed. The second generation type is prepolymers, which are commonly belonged to the complex urethane acrylates, polyester acrylates, polyether acrylate and acrylated oils (Allen, 1996).

There are several advantages of these technologies include faster curing time, coating quality and low solvent levels. The main advantage of using UV radiation to initiate the chain reaction lies in the very high polymerization rates that can be reached under intense illumination, so that the transformation from liquid phase to solid phase take place within a fraction of a second (Burak, 1997). Concern for the environment is beginning to permeate all aspects of life and business. Governments around the world are imposing strict control involving volatile organic compound (VOC) emissions. UV curing complies with all of these environmental regulations. The solvent-free and usually VOC-free, depending on the volatility of monomers used have increased the popularity and growth of UV technology.

UV emission is divided into 4 groups based on wavelength/energy and ability to interact with matter. Table 2.1 shows the categories of ultraviolet (UV):

Table 2.1: Categories of Ultraviolet (UV)

UV range	**Application**
UVA (315 – 400 nm)	Backlight. Used for Low energy UV polymerization reactions, also for fluorescent inspection purpose.
UNB (280 – 315 nm)	Used with UVA for polymerization. The most energetic region of sunlight. For accelerated light aging of materials. Responsible for sun tanning
UVC (200 – 280 nm)	Used for rapid surface cure of UV links and coatings. Sterilization and germicidal applications.
VUV (100 – 200 nm)	Vacuum UV. Can only be used in vacuum. Minor commercial importance.

2.2 Polymerization of UV curable system

Photophysical and photochemical process can be classified as the excited state which can undergo a variety of transitions. The contrast between photophysical and photochemical is the capability to produce new chemical compounds. According to Dietliker (1991), photophysical process does not produce new chemical compounds, but it interconverts excited states with each other or excited states with ground states. However, photochemical process can produce new chemical species and produce different chemical compounds from the starting material.

Dietliker (1991), also reported that a photoinitiator (photoinitiator system) can be considered to be a molecule or combination of molecules. When a photoinitiator is exposed to irradiation, it can initiate polymerization at a faster rate than systems without photoinitiator. Basically, no polymerisation would occur in UV curable system without the presence of a photoinitiator. Most of the photoinitiation processes involve a uni- or bimolecular process. This applied to both free radical and cationic photoinitiations (Dietliker, 1991).

There are two main stages of photochemical process, which are;

A) Primary Process

B) Secondary process

2.2.1 The primary process

Photochemical reactions can only occur with the occurrence of absorption of a photon (Dietliker, 1991). Thus, absorption is very important in primary process. The absorption of a photon from the incident radiation is the first stage in any UV/Visible light curing system. The absorption should happen before there is a possibility of reaction occurring. Photoinitiators absorb the photons and transfer the energy to the electronic structure of a molecule. This excitation of the electrons, either directly or by reaction with another molecule can ultimately result in the formation of free radicals or a cations. Therefore, electronic transitions are the heart of the efficient functioning of photoinitiators or photoinitiating system (Dietliker, 1991).

2.2.2 The secondary process

A polymerization can only be initiated after the initial excitation which produces initiating species. This occurs by chemical reaction from the excited state (the photoreaction), which is possibly followed by thermal reaction steps. According to Dietliker (1991), the absorption of a photon, as well as the different deactivation and state interconversion process will not change the chemical constitution of the molecule and they are named as photophysical processes. The reaction occurs from the excited state with a new chemical constitution in a fragmentation reaction or with a new number of electrons is an electron transfer process. Thus, it produces a chemically new species and it is termed the primary photochemical reaction and followed by the thermal reactions, which is the secondary, or dark reactions. However, there are many photochemical reaction mechanisms can occur which are;

- Unimolecular reactions (type I)
- Bimolecular reactions (type II)
- Energy transfers, followed by unimolecular or bimolecular reactions.

2.2.2 (a) Unimolecular reactions

Unimolecular reactions is defied as a chemical reaction that involving one molecular species as a reactant. In unimolecular photoinitiations, a photoinitiator involves in direct fragmentation and norrish reactions.

(i) Direct Fragmentation

Fragmentation or homolitic scission is defined as a process where a photoinitiator containing a bond with lower dissociation energy than the excited state dissociates and forms a reactive species (Dietliker, 1991). These types of photoinitiator are known as type I photoinitiators and both free radical and cationic photoinitiators can undergo similar mechanism. Nevertheless, the energy of dissociation bond must not be too low that the bond readily fragments at the temperature at which an initiator is usually exposed. In order to reach to an optimum photoreactivity, a photoinitiator must have good thermal stability (Dietliker, 1991).

ii) Norrish Reactions

In unimolecular photoinitiations, the carbonyl group is at the heart of many photochemical reactions of the interest to UV or visible light which induces curing by free radical mechanisms. An excited organic carbonyl compounds can undergo a variety of photochemical reactions which is shown in Figure 2.1 (Dietliker, 1991).

This type of reaction is subdivided in to Norrish type I and Norrish type II (Figure 2.2) reactions and the reactions are named after Ronald George Wreford Norrish. According to Dietliker, homolitic cleavage occurs between the carbonyl group and adjacent α – carbon. (Figure 2.1 Norrish type I reaction). Norrish type II reaction involves the abstraction of hydrogen atom from the γ-position of carbonyl group, resulting in a 1,4-biradical as the primary photoproduct. Based on the structure, it will either undergo a fragmentation reaction (Figure 2.2 type II fragmentation) to give an enol and an alkene or ring closure to give an oxetane.

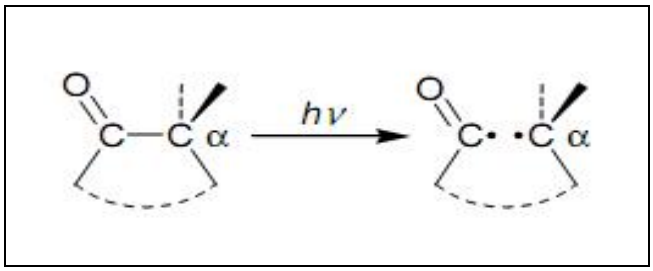

Figure 2.1: Norrish type I reaction

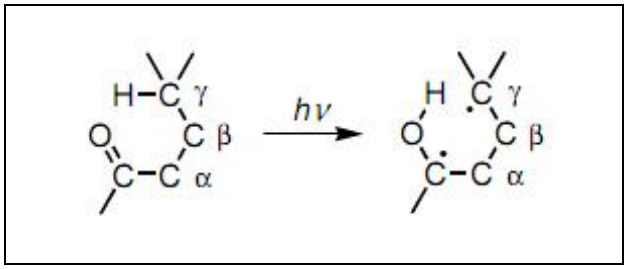

Figure 2.2: Norrish type II reaction

Therefore, only Norrish types I fragmentation produces the radicals for initiation of polymerization in unimolecular photoreactions. Whereas the Norrish type II reaction also produces radicals but mostly for initiation and other processes.

2.2.2 (b) Bimolecular reactions

Dietliker (1991) also reported that, bimolecular reaction (type II photoinitiators) is an initiating system whereby a molecule reacts with another molecule to produce an initiating species. Owing to the competitive light absorption of a formulation in the spectral area useful for excitation of the initiator, the direct excitation might be difficult under certain conditions. Therefore, the light absorbing molecule is named as photosensitizer and the second compound is the coinitiator. This photosensitier or coinitiator (or both) may produce initiating species and it is also possible to activate a photoinitiator system via energy or electron transfer from a photosensitizer molecule (Dietliker, 1991).

(i) Hydrogen Abstraction

Bimolecular process is another type of to produce radical from carbonyl compounds for the initiation of a polymerisation. According to Dietliker (1991), hydrogen abstractor can abstract a hydrogen atom in order to produce some aromatic ketones from free radicals.

2.3 UV free radical curing systems

UV photochemical process is induced by absorption of high intensity UV light by a photoinitiator to produce free radicals to initiate curing process. This is known as free radical polymerization. The active radicals will then add to the monomer, inducing a chain-growth process. As noted above, free radical UV curable system consists of three steps- i.e. initiation, propagation and termination. There are two reactions involve in the initiation step. The first step is the production of free radicals and the second reaction is the initiation step involves the addition of free radical to a monomer molecule (Mehnert et al., 1998).

Chain propagation involves the growth of monomer (M, which shows in Figure 2.3) by the successive addition of large numbers of monomer molecules. A new radical is being created after each addition. The propagation or growing of chain continues until it reaches a point that the propagation reaction is terminated due to annihilation of the radical canter of the propagation chain. Figure 2.3 shows the various steps in a photoinitiated polymerisation.

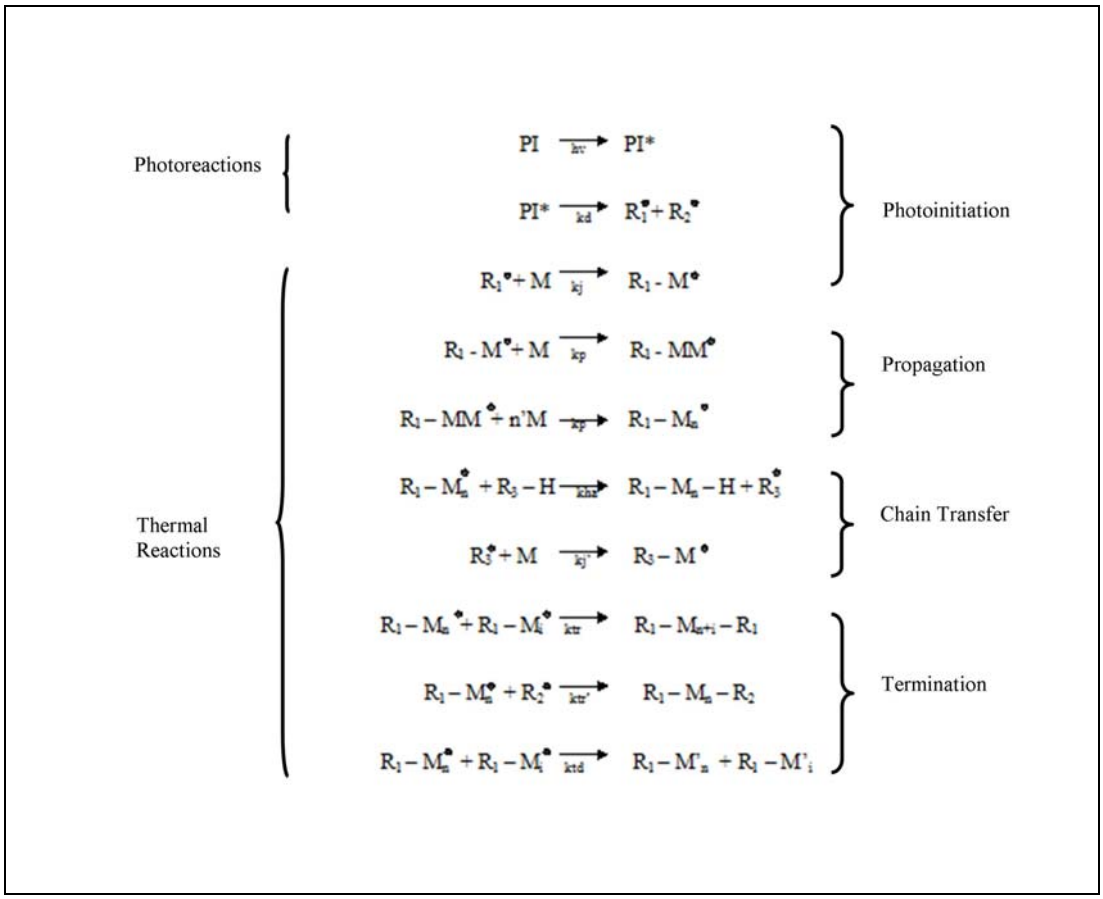

Figure 2.3: Various steps in a photoinitiated polymerisation

Where by;

PI = photoinitiator

PI* = excited photoinitiator

$R_1^{\bullet}$, $R_2^{\bullet}$ = radical fragments of the photoinitiator

$R_3 - H$ = hydrogen donor

M = Monomer

2.4 UV cationic curable systems

Cationic polymerization is an ionic process involving highly reactive, positively charged polymerizing centres. Upon exposure to UV light, the cationic photoinitiator generates Lewis acid (Mehnert et al., 1998).

Lewis acids can initiate the cationic polymerization. These electrophilics are electron acceptors and capable in generating carbonium ion which can initiate polymerization. UV cationic curable systems are not inhibited by oxygen but are inhibited by base because it involves positively charged species and not unpaired electrons. UV cationic curable systems show a wide range of properties which include good adhesion, impart resistance, chemical resistance and hardness. A 'dark cure' phenomenon is defined as the acid catalyst generated from the photoinitiator continues to be active after UV curing. As a result, the conversion of reactions and the cross linking can continue. This can even last days after UV irradiation (Mehnert et al., 1998).

2.5 Photoinitiator

Photoinitiator is used to absorb light energy and transforms into active species, such as radicals or ions. The photo physical and photochemical behaviour of the photoinitiator is extremely important in controlling its reactivity. Good photoinitiators should satisfy the following requirements (Allen, 1996).

- High absorptivity in the region of activation, which depends upon the application and light source used

- High quantum output for free radical formation
- Adequate solubility in the resin system used
- High storage stability
- No odour or yellowing and
- Non-toxicity, low cost and ease of handling.

Generally there are two classes of photoinitiators that meet these requirements, which are type I photoinitiators and type II photoinitiators. This classification is made based on the process of photofragmentation.

2.5.1 Type I photoinitiators

According to Dietliker (1991), most of the types I photoinitiators are aromatic carbonyl compounds containing suitable subsistent which can facilitate direct photofragmentation and producing radicals. An example for the type I photoinitiators are shown in. The fragmentation reactions occur at a bond adjacent to the carbonyl group (α-cleavage), at a bond in the β-position (β-cleavage) or in weak bonds. However, the most important fragmentation in photoinitiator molecules is the α-cleavage of the carbon-carbon bond between the carbonyl group and the alkyl residue in alkyl aryl ketones, which is known as the Norrish type I reaction (Dietliker, 1991).

2.5.2 Type II

Bimolecular reaction [Type II] involves two main reaction pathways, such as hydrogen abstraction by the excited initiator and photoinduced electron transfer, followed by fragmentation. Type II reaction is the abstraction of a hydrogen atom from γ position by carbonyl group and resulting in primary photoproduct which reaction pathway will be followed after absorption of a photon (Dietliker, 1991). Diaryl ketones do not undergo α-cleavage reacting when it was triplet excited. Nevertheless, they can extract a hydrogen atom from a suitable hydrogen donor. There are three main factors relating to the hydrogen abstraction (Dietliker, 1991);

- The triplet state configuration of ketone
- The triplet state energy of the ketone
- The bond strength of the carbon hydrogen bond to be broken

2.6 UV lamps

According to Mehnert et al. (1998), to induce UV curing, light must be absorbed by a suitable photoinitiator, which is part of the radiation curable formulation. The choice of the light source determines the rate of chemical conversion in a curing reaction with a given chemical formulation (Mehnert et al., 1998).

2.6.1 Medium pressure mercury arc lamps

This lamp is the most broadly used for UV curing applications, medium pressure mercury arc lamps produces almost 29% UV over a wide spectral range (200-400nm) and is the most efficient of the available high output lamps in converting electrical power to UV energy (Braithwaite, 1991). In addition, it is extremely versatile being produced in any length from a few centimeters up to 2.5 meters (Braithwaite, 1991).

2.7 Lignin

Lignin has been classified as one of the resources having potential as replacement for petroleum based chemical. Lignin is a natural polymeric material, which serves as a natural binder for cellulose fiber. It is a highly branched polymer with wide varieties of functional groups that are believed to be capable of providing active site for chemical interactions. There are various types of lignin available in market, such as kraft lignin, lignosulfonates, organosolv lignin etc. Lignin is non-toxic and extremely versatile in performance and qualities. This makes it popular in many industrial applications (Tejado et al., 2008). However, the potential of lignin application are not discovered and almost all is burned to generate energy (Mansouri and Salvadó, 2006). Traditionally, lignin was treated as industrial waste from the process of pulping of wood, was mainly used as fuel (Lora and Glasser, 2002).

Lignin is characterized as a polyphenolic material having an amorphous structure that arises from an enzyme-initiated dehydrogenative polymerization of p-coumaryl, coniferyl and sinapyl alcohols. Consequently, lignin structure is defined into only two components; which is aromatic part and C3 chain. Additionally, the hydroxyl group (OH) for both phenolic and alcoholic hydroxyl groups in lignin is the only usable reaction site (Abe et al., 2009).

Lignin is a macromolecular component of cell wall for wood and other lignocellulosic materials. Fibers, vessels and cells are bonded by lignin. According to Axelrod and De Pree (2003), lignin concentration in wood substance is greatest in the middle lamella, decreasing in concentration through the cross section of the fiber, reaching a concentration of about 12% at the inner layer of the fiber adjacent to the

fiber cavity, or lumen. It connects cells in order to harden the cell walls of xylem tissues. Lignified cell walls are considered important to the stems of woody plants and the conductive xylem tissues for water transport as they strengthen the tissues and decrease the permeability of cell walls. According to Browning, (1967) the content and structure of lignin is different in hardwood and soft wood. Throughout the growth of the cells, lignin is integrated as the last constituent into the cell walls interpenetration fibers, thus strengthening the cell wall.

2.7.1 Classification of lignin

There are three different types of lignin classification. However, the classification of lignin has so far received extensive attention. Lignin has been classified to gymnosperm or softwood lignin, angiosperm wood or hardwood lignin and grass lignin. These three types of lignins are distinctive in nitrobenzene oxidation product. Firstly, gymnosperm lignin produced mainly vanillin with some p-hydroxybenzaldehyde; secondly, angiosperm wood lignin produced both syringaldehyde and vanillin and thirdly significant amount of all three aldehydes are obtained from grass lignin (Sarkanen, 1971).

However, Gibbs has carried out another way to classify lignin in plant kingdom into two major classes only, which is “guaiacyl lignin” and “guaiacyl-syringyl lignin” based on their Mäule reaction. All angiosperm lignin and grass lignin belong to guaiacyl-syringyl lignin. Consequently, guaiacyl-syringyl lignin may be introduced by their positive Mäule reaction and always yields significant amount of syringaldehyde in nitrobenzene oxidation. In contrast, most of the gymnosperms

have guaiacyl lignin and is distinguished by a negative Mäule reaction (Browning, 1967).

2.7.2 Methods of isolation of lignin

Lignin is usually categorized according to isolation procedures. Basically there are three large groups of lignin isolation methods which can be classified as (Browning, 1967):

- Isolation of lignin in solution
- Lignin as residue
- Lignin as derivatives.

2.7.3 (I) Isolation of lignin in solution

The easier process of lignin isolation is neutral solvent extraction, which does not react with lignin. However, only a small portion of protolignin is soluble in neutral solvent. The best way to obtain unchanged lignin is by Bjorkman's procedure of vibratory milling and subsequent extraction with aqueous dioxine and this method is named as Milled Wood Lignin (MWL). Though MWL is not similar with the lignin insitu and yet still considered as suitable material for further investigation (Browning, 1967).

2.7.4 (II) Isolation of lignin as residue

Isolation of lignin as residue is employed only for lignin determination and not for determining the structure. Under this type of isolation method, cellulose is dissolved and lignin is produced as a residue. Consequently, the structure and

properties of lignin are changed. Thus this method is not suitable for determining the lignin structure (Browning, 1967).

2.7.5 (III) Isolation as derivatives

The wood is treated with reagents that react with lignin and form soluble products. Thus, lignin can be separated from the polysaccharides or their reaction products through solubility (chemical behaviour) (Browning, 1967).

2.7.5. a) Organosolv Lignins

Alcohol lignin

An alcohol soluble lignin is produced after the reaction of lignin and alcohol with the presence of mineral acids.

Phenol lignin

A soluble phenol lignin is formed from the reaction of lignin and phenol, in the presence of hydrogen chloride. The phenol lignin can be extracted from the wood (Browning, 1967).

Thiolycolic acid lignin

According to Browning (1967), thio compounds, such as thioglycolic acid in the presence of hydrochloric acid, condense very easily and under relatively mild conditions with lignin to form alkali- and dioxane-soluble lignothioglycolic acids in high yields and with a readily reproducible chemical composition. Benzyl alcohol

groups in the lignin molecule react with the thioglycolic acid. However, the other functional groups of the molecule also involve in the reaction (Browning, 1967).

Acetic acid lignin

Organic acids can be used to extract the lignin from wood with the presence of small amount of mineral acids. Extraction can be carried out by acetic acid with H_2SO_4, HCL or $MgCl_2$ to give acetic acid lignin (Browning, 1967).

2.7.5.b) Reactions with inorganic reagents

Lignosulphonates

Majority of lignin in wood can be dissolved by solutions of sulphurous acid and its salts. The lignin reacts to form water-soluble lignosulfonates, and the sulfonation reaction forms the basis of the important commercial sulfite pulping process which are (Browning, 1967);

- Acid sulphite process, which uses a bisulphite + excess of three H_2SO_3.
- Bisulphite process uses bisulphite without substantial excess of free H_2SO_3.
- Neutral sulphite process uses sodium sulphite solution buffered at pH 7.00.

Alkali lignin

When wood is heated with NaOH solution at 160^{o}C - 180 ^{o}C under pressure, most portion of the lignin is removed. This is the basis of commercial soda pulping process (Browning, 1967).

Thiolignin

Thiolignin is produced when wood is digested with sodium sulphide solution or a mixture of sodium sulphide and NaOH (Browning, 1967).

2.8 Lignin as Bio-Resource

Lignin is one of the most important bio-resources as the raw material for the synthesis of environmentally compatible polymers (Abe et al., 2009). Basically, 30% of wood constituents are lignin, where it is non-toxic and multifarious in performance. According to Abe et al. (2009), the production of lignin in pulping process as a by-product is over 30 million tons per year worldwide (an estimate). Traditionally most of the lignin is burnt as fuel immediately after production and commercial lignins are obtained as by-products of the pulping or bio-ethanol industries (Abe et al., 2009).

There are three major structures of lignin, which are 4-hydoxyphenyl (1), guaiacyl (2) and syringyl (3) structures which are conjugated to produce a three-dimensional lignin polymer in the process of radical-based lignin biosynthesis. Lignin is physically and chemically heterogeneous material, however lignin does not have a regular structure like cellulose and its exact chemical structure is still unknown. Lignin molecule has more than two hydroxyl groups, therefore lignin can incorporate into lignin-based polyurethane derivatives and polycaprolactones (PCL) derivatives and epoxy resins by using the hydroxyl group as the reaction site (Abe et al., 2009).

Lignin is obtained as the byproduct of pulp and paper industry and bio-ethanol production. However, wood powder can be directly used as fillers for lignin-based polyurethane composites. It can be said that it is necessary to use industrial lignin due to the effective and cost-saving utilization of lignin (Abe et al., 2009).